

# Compatibility of Correlation-Consistent Basis Sets with a Hybrid Hartree–Fock/Density Functional Method

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**ABSTRACT:** The present study examines the feasibility of combining the correlation-consistent basis sets developed by Dunning and coworkers with the hybrid Hartree–Fock/density functional method B3LYP. Furthermore, extrapolation to the complete basis set (CBS) limit minimizes errors due to the presence of an incomplete basis set and can act as a rigorous test of the limitations of the B3LYP method. Equilibrium geometries, energies, and harmonic vibrational frequencies were determined for a series of well-studied, yet computationally challenging, small inorganics and their respective ions. The results were then extrapolated to the CBS limit, where applicable, and compared to experiment. It was found that a union between the hybrid Hartree–Fock/density functional B3LYP method and Dunning’s augmented correlation-consistent basis sets gave results that were comparable to molecular orbital methods that explicitly account for electron correlation. Furthermore, the minimum basis set necessary to attain reasonable results for the systems studied was aug-cc-pVTZ. Upgrading to the aug-cc-pVQZ level and subsequent

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extrapolation to the CBS limit further improved the overall agreement with the experiment. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 207–216, 1999

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## Introduction

One of the main limitations of the accuracy of electronic structure calculations is how to account for the effects of electron correlation.<sup>1,2</sup> There are two categories of electron correlation, which were first defined by Sinanoglu.<sup>3</sup> The first is a nondynamical or near-degeneracy correlation that includes effects such as space and spin polarization resulting from contributions to the ground state from partially occupied nonvalence orbitals.<sup>1,4</sup> It arises from an interaction between the electronic ground state and low-lying excited states and causes a net lowering of the energy.<sup>5</sup> Taking into account the contribution of low-lying excited states involving only one excited electron, the use of multiconfiguration calculations (such as configuration interaction, CASSCF, or coupled cluster methods) can adequately account for this type of electron interaction.<sup>1</sup> Although density functional (DF) theory does not handle the problem of nondynamical electron correlation well, some attempts have been made to modify the Hartree–Fock (HF) term in hybrid HF/DF calculations to include limited configuration interaction in an attempt to account for this problem.<sup>6–8</sup>

The second category of effects due to electron correlation is dynamical correlation effects that consist of the instantaneous correlation in the motions of electrons at short interelectronic distances.<sup>4,6</sup> Multiconfiguration calculations can account for these effects in much the same way as nondynamical correlation effects, the only difference being that two or more electrons must occupy nonvalence orbitals. This phenomenon is well represented by the local density approximation in DF theory.<sup>6,9,10</sup> The result is further improved by the addition of a gradient-corrected (nonlocal) correlation correction term to the DF energy expression.<sup>11</sup>

Recently, attempts to account for the effects of electron correlation were extended to basis set development.<sup>1,12–19</sup> Dunning coworkers devel-

oped a family of correlation-consistent basis sets that have three important characteristics:

1. they include functions with high angular momenta,  $(d, f, g, \dots)^{15–19}$ ;
2. they consist of basis functions that can be grouped into sets with each function in the set lowering the correlation energy by a similar amount<sup>15–19</sup>; and
3. the basis functions are optimized to describe correlation effects in atoms, but also describe correlation effects in molecules as well.<sup>18,19</sup>

A recent study by Scheiner and colleagues<sup>20</sup> uses SVWN, BLYP, BPW91, and B3PW91, along with Dunning et al.'s aug-cc-pVTZ basis set<sup>1,21,22</sup> to calculate geometries, dipole moments, atomization energies, and heats of reaction for the G1 set of molecules. The authors discuss statistical agreement with an experiment for the geometries and dipole moments but do not discuss electron affinities, spin densities, or vibrational frequencies. Furthermore, they use only the triple-zeta basis set and employ the uncontracted form of the basis set to approximate basis set saturation. The present study explores the usefulness of a marriage between the hybrid HF/DF method B3LYP and the set of augmented correlation-consistent basis sets developed by Dunning and coworkers.<sup>1,21,22</sup> Calculations were performed to determine the equilibrium bond lengths, bond angles, electron affinities, dipole moments, atomization energies, and harmonic vibrational frequencies for a number of well-studied inorganic di- and triatomics. The results were then extrapolated to the CBS limit<sup>23–25</sup> and compared to experimental and calculated values found in the literature that utilize the coupled-pair functional approach (CPF),<sup>26,27</sup> which attempts to explicitly account for electron correlation. Furthermore, extrapolation of results to the CBS limit minimizes errors due to an incomplete basis set and tests the limitations of the B3LYP method.

## Computational Methods

All calculations were performed using the Gaussian 94<sup>28</sup> suite of quantum chemistry programs and utilized hybrid HF/DF theory.<sup>11,29–31</sup> The method tested was a variant of Becke's 3 parameter hybrid HF/DF method,<sup>11,32</sup> which has the form

$$E = AE_x^{\text{Slater}} + (1 - A)E_x^{\text{HF}} + B\Delta E_x^{\text{Becke}} + E_C^{\text{VWN}} + C\Delta E_C^{\text{nonlocal}},$$

where  $E_x^{\text{Slater}}$  and  $E_x^{\text{Becke}}$  refer to Slater's local spin density approximation<sup>33</sup> and Becke's gradient-corrected expression<sup>34</sup> for exchange energies,  $E_x^{\text{HF}}$  refers to an HF energy operator, and  $E_C^{\text{VWN}}$  represents Vosko, Wilk, and Nusair's local correlation functional.<sup>35</sup> The parameters  $A = 0.20$ ,  $B = 0.72$ , and  $C = 0.81$  were obtained empirically to reproduce experimental energies, ionization potentials, and electron affinities for certain small molecules<sup>36</sup> using Perdew's 1986 gradient-corrected functional (P86)<sup>37</sup> for the nonlocal term in the above expression. However, for this study the nonlocal portion, which is the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP),<sup>38</sup> was chosen to replace that of Perdew. While the parameters  $A$ ,  $B$ , and  $C$  are specific to B3P86, tests by Bauschlicher and Partridge<sup>39,40</sup> show that one can obtain thermochemical accuracy by using these with the LYP functional as well. Furthermore, the B3LYP functional<sup>11,32,41</sup> reproduces molecular

properties, including geometries and frequencies,<sup>42–56</sup> electron affinities,<sup>57</sup> and spin properties,<sup>44–49,51,52,55,56,58–60</sup> of numerous polyatomic molecules, radicals, and ions. In concert with the above method, Dunning et al.'s correlation-consistent cc-pVXZ ( $X = D, T, Q, 5$ ) basis sets augmented with one diffuse function of each angular momentum type ( $s, p, d, f, \dots$ ) were used.<sup>1,21,22</sup>

In addition, the results were extrapolated to the CBS limit. To achieve this, data obtained from these calculations was fit to the exponential function

$$f(x) = f(\infty) + Ae^{-(Bx)},$$

where  $x = 2, 3, 4$ , and  $5$  for double-, triple-, quadruple-, and quintuple zeta basis sets, respectively,<sup>23,24</sup> using the Nonlinear Regression Analysis Program (NLREG) shareware package.<sup>61</sup> This equation is one of several proposed extrapolation schemes.<sup>25</sup>

## Results

A study of the NO/NO<sup>+</sup> system using the hybrid HF/DF B3LYP method and Dunning's correlation-consistent aug-cc-pVXZ ( $X = D, T, Q, 5$ ) was done to confirm the convergence of calculated values with increasing basis set size. The results (Table I) show that as the basis set size was increased from the double-zeta to triple-zeta level there were marked changes in structural parameters and electron affinities. However, increasing the basis set beyond the quadruple-zeta level up to

**TABLE I.** Comparison of Calculated and Experimental Bond Distances (Å) and Electron Affinities (kcal/mol) for NO/NO<sup>+</sup> System.

	Parameter	Basis Set				Expt <sup>a</sup>
		aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	
NO	Bond length	1.154	1.146	1.144	1.144	1.151 <sup>b</sup>
		—	—	(1.144)	(1.144)	
NO <sup>+</sup>	Bond length	1.068	1.057	1.056	1.056	1.063 <sup>b</sup>
		—	—	(1.056)	(1.056)	
	Electron affinity	225.9	223.3	223.0	223.0	213.5 ± 0.1
		—	—	(223.0)	(223.0)	

An extrapolation to the CBS limit is given in parentheses.

<sup>a</sup> References 64–67.

<sup>b</sup> Experimental uncertainty < 0.001 Å.

quintuple-zeta elicits negligible changes in these quantities. One can also see that there is no marked change in the extrapolation of these values to the CBS limit by adding the fourth data point obtained from the quintuple-zeta basis set, and this further increase in basis set size is not worth the subsequent demand on computational resources.

Tables II and III provide a comparison between experimental structures, structures calculated using the CPF method, and those obtained from this study. Substantial deviation between calculated and experimental bond distances were found for most of the systems studied, and an average of 0.015 Å separated the extrapolation to the CBS limit from the experiment. The Cl<sub>2</sub> and Cl<sub>2</sub><sup>-</sup> species posed the greatest challenge to the theory, and the results deviated from the experimental bond distances by 0.026 and 0.087 Å, respectively. A similar difficulty was encountered in a study by Eberson and coworkers,<sup>62</sup> and it was attributed to signifi-

cant electron correlation in Cl<sub>2</sub><sup>-</sup>; it is best described as a complex between a chlorine atom and a chloride ion. Excluding the results for Cl<sub>2</sub> and Cl<sub>2</sub><sup>-</sup>, the average deviation from experimental bond lengths drops to 0.009 Å; many of the calculated values fell within the experimental error. These values were compared to average deviations from the experiment of 0.011 Å for previous calculations<sup>62</sup> using the CPF method,<sup>26,27</sup> which explicitly includes corrections for electron correlation. A similar agreement was found when comparing calculated and experimental bond angles. Excluding the more troublesome NO<sub>2</sub>, SO<sub>2</sub><sup>-</sup>, ClO<sub>2</sub>, O<sub>3</sub>, and O<sub>3</sub><sup>-</sup> systems gives an average deviation from the experiment of 0.2°. Including the O<sub>3</sub> and O<sub>3</sub><sup>-</sup> species, which require multi-reference CI methods, raised the average deviation to 0.6°. This compares well with the aforementioned CPF study that attained average deviations of 0.4° when excluding O<sub>3</sub>, O<sub>3</sub><sup>-</sup>, NO<sub>2</sub>, SO<sub>2</sub>, and ClO<sub>2</sub>; 0.6° when O<sub>3</sub> and O<sub>3</sub><sup>-</sup> were in-

TABLE II. Comparison of Experimental and Calculated Bond Lengths (Å) for Selected Di- and Triatomics.

	Basis Set			Complete Basis Set Limit Extrapolation	Calc <sup>a</sup>	Expt <sup>b</sup>
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ			
NO	1.154	1.146	1.144	1.144	1.153	1.151 <sup>c</sup>
NO <sup>+</sup>	1.068	1.057	1.056	1.056	1.061	1.063 <sup>c</sup>
NO <sub>2</sub> <sup>-</sup>	1.261	1.255	1.254	1.254	1.258	1.250 ± 0.02
NO <sub>2</sub>	1.198	1.191	1.190	1.190	1.199	1.194 <sup>c</sup>
NO <sub>2</sub> <sup>+</sup>	1.125	1.116	1.115	1.115	1.117	1.104 ± 0.01
NO <sub>3</sub>	1.185	1.174	1.173	1.173	1.179	1.182 <sup>c</sup>
NO <sub>3</sub> <sup>-</sup>	1.190	1.179	1.178	1.178	1.182	1.188 <sup>c</sup>
O <sub>2</sub>	1.209	1.206	1.204	1.200	1.219	1.208 <sup>c</sup>
O <sub>2</sub> <sup>-</sup>	1.344	1.343	1.340	DNF	1.362	1.347 ± 0.002
O <sub>3</sub>	1.256	1.255	1.252	DNF	1.283	1.278 ± 0.002
O <sub>3</sub> <sup>-</sup>	1.350	1.351	1.347	DNF	1.361	1.341 ± 0.03
SO <sub>2</sub>	1.484	1.451	1.442	1.439	1.440	1.431 <sup>c</sup>
SO <sub>2</sub> <sup>-</sup>	1.567	1.529	1.519	1.515	1.520	1.523 ± 0.02
ClO	1.620	1.591	1.583	1.579	1.587	1.569 ± 0.004
ClO <sup>-</sup>	1.741	1.707	1.698	1.694	1.702	1.673 <sup>c</sup>
ClO <sub>2</sub>	1.541	1.500	1.488	1.483	1.484	1.470 ± 0.014
ClO <sub>2</sub> <sup>-</sup>	1.639	1.598	1.586	1.581	1.587	1.59 ± 0.05
Cl <sub>2</sub>	2.046	2.024	2.017	2.014	1.998	1.988 ± 0.03
Cl <sub>2</sub> <sup>-</sup>	2.732	2.712	2.708	2.707	2.59	2.62 ± 0.03
Ave dev	0.031	0.018	0.015	0.012	0.011	—

DNF, the data did not fit the extrapolation function; Ave dev, the average absolute deviation from the experiment.

<sup>a</sup> Reference 62.

<sup>b</sup> References 64 and 66–86.

<sup>c</sup> Experimental uncertainty is either unknown or < 0.001 Å.

**TABLE III.**  
**Comparison of Experimental and Calculated Bond Angles (°) for Selected Triatomics.**

	Basis Set			Complete Basis Set Limit Extrapolation	Calc <sup>a</sup>	Expt <sup>b</sup>
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ			
NO <sub>2</sub> <sup>-</sup>	116.6	116.9	116.9	116.9	116.5	117.5 ± 2
NO <sub>2</sub>	134.2	134.5	134.4	DNF	133.4	133.9 <sup>c</sup>
NO <sub>2</sub> <sup>+</sup>	180.0	180.0	180.0	180.0	180.0	180.0
N <sub>3</sub>	180.0	180.0	180.0	180.0	180.0	180.0
N <sub>3</sub> <sup>-</sup>	180.0	180.0	180.0	180.0	180.0	180.0
O <sub>3</sub>	118.1	118.3	118.3	118.4	116.7	116.8 ± 0.5
O <sub>3</sub> <sup>-</sup>	115.2	115.4	115.5	115.5	115.4	112.6 ± 2
SO <sub>2</sub>	117.5	118.2	118.7	119.4	118.8	119.3 <sup>c</sup>
SO <sub>2</sub> <sup>-</sup>	114.0	113.9	114.0	DNF	113.7	115.63 ± 2
ClO <sub>2</sub>	118.8	116.8	117.0	DNF	116.9	116.5 ± 2.5
ClO <sub>2</sub> <sup>-</sup>	114.6	113.8	113.7	113.7	113.2	1.59 <sup>c</sup>
Ave dev	1.0	0.8	0.8	0.6	0.7	—

DNF, the data did not fit the extrapolation function; Ave dev, the average absolute deviation from the experiment.

<sup>a</sup> Reference 62.<sup>b</sup> References 64 and 66–86.<sup>c</sup> Experimental uncertainty is either unknown or < 0.01°.

cluded; and 0.7° when all triatomics were taken into account. Finally, while NO<sub>2</sub>, SO<sub>2</sub><sup>-</sup>, and ClO<sub>2</sub> data did not allow extrapolation to the CBS limit, it should be noted that the results of this study for these molecules using the aug-cc-pVQZ basis set

showed a deviation from the experiment similar to the CPF study.<sup>62</sup>

Table IV compares calculated and experimental dipole moments for the molecules studied. The results show qualitative agreement with experi-

**TABLE IV.**  
**Comparison of Calculated and Experimental Dipole Moments (D) for Selected Small Molecules.**

	Basis Set				Complete Basis Set Limit Extrapolation	Expt
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z		
NO	0.070	0.097	0.101	0.102	0.102	0.159 ± 0.1% <sup>a</sup>
NO <sup>+</sup>	0.418	0.399	0.397	0.396	0.396	—
NO <sub>2</sub>	0.612	0.606	0.606	—	0.606	0.316 ± 0.1% <sup>b</sup>
NO <sub>2</sub> <sup>-</sup>	0.668	0.664	0.660	—	DNF	—
O <sub>3</sub>	0.768	0.782	0.786	—	0.788	0.534 ± 0.1% <sup>c</sup>
O <sub>3</sub> <sup>-</sup>	1.251	1.259	1.263	—	1.266	—
SO <sub>2</sub>	2.113	2.004	1.985	—	1.891	1.633 ± 0.1% <sup>c</sup>
SO <sub>2</sub> <sup>-</sup>	2.069	1.863	1.776	—	1.712	—
ClO	1.218	1.257	1.262	—	1.262	1.262 ± 0.1% <sup>a</sup>
ClO <sup>-</sup>	2.476	2.400	2.356	—	2.294	—
ClO <sub>2</sub>	2.097	2.038	1.990	—	1.787	0.780 ± 0.1% <sup>d</sup>
ClO <sub>2</sub> <sup>-</sup>	2.777	2.654	2.585	—	2494	—

DNF, the data did not fit the extrapolation function.

<sup>a</sup> Reference 87.<sup>b</sup> Reference 88.<sup>c</sup> Reference 89.<sup>d</sup> Reference 90.

ment for most of the systems studied. However, the calculated dipole moment of ClO<sub>2</sub> is dramatically overestimated compared to experiment.

Table V compares calculated and experimental electron affinities for selected small inorganic molecules. Of note are the exemplary results for the electron affinities of NO<sub>2</sub><sup>+</sup>, ClO, and N<sub>3</sub>, which are all accurate to within 0.8 kcal/mol. However, not all systems shared this success. Due to the need for MRCI methods for the O<sub>3</sub>/O<sub>3</sub><sup>-</sup> and Cl<sub>2</sub>/Cl<sub>2</sub><sup>-</sup> systems, computational difficulties were encountered while computing their energies, leading to large errors in the calculated electron affinities. Furthermore, the calculated electron affinities for oxygen and ozone did not fit the functional form for extrapolation to the CBS limit. Omitting the oxygen, ozone, and chlorine systems, the average separation of calculated and experimental electron affinities is 3.9 kcal/mol. Taking the values for the Cl<sub>2</sub>/Cl<sub>2</sub><sup>-</sup> system into account raises the average deviation to 4.7 kcal/mol. These errors compare to 3.6 and 3.2 kcal/mol for similar data from Ebersson et al.'s study where MRCI was used for troublesome molecules.<sup>62</sup>

A comparison of calculated and experimental atomization energies for a set of small inorganic

molecules is shown in Table VI. Unfortunately, the data did not fit the functional form used to extrapolate to the infinite basis set. Still, with the exception of SO<sub>2</sub>, all values calculated with the aug-cc-pVQZ basis set were within 5.5 kcal/mol. Including the questionable results for SO<sub>2</sub>, the average absolute deviation from the experiment was still only 4.6 kcal/mol at this level. This compares with the well-documented G1 and G2 methods,<sup>63,98,99</sup> which show average absolute deviations from the experiment of 2.9 and 1.9 kcal/mol, respectively, for this set of molecules, but at a higher price in computational resources. It should also be noted that these studies encountered similar difficulties in attempting to calculate the atomization energy of SO<sub>2</sub>.<sup>99</sup> By excluding SO<sub>2</sub> the deviations drop to 3.4 kcal/mol for the present study, 2.2 kcal/mol for G1, and 1.4 kcal/mol for G2.

Table VII compares experimental vibrational frequencies for the small inorganics with those calculated using the B3LYP method and aug-cc-pVXZ basis set, where X = D, T, Q, and 5. Although the calculated vibrational frequencies do not fit the functional form for extrapolation to the infinite basis set, the results obtained using the aug-cc-pVQZ basis set show good agreement with

**TABLE V.** Comparison of Calculated and Experimental Electron Affinities (kcal / mol) for Variety of Selected Small Molecules.

	Basis Set			Complete Basis Set Limit Extrapolation	Calc <sup>a</sup>	Expt <sup>b</sup>
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ			
NO <sup>+</sup> <sup>c</sup>	226.6	224.1	223.8	223.8	213.1	213.5 (0.1)
NO <sub>2</sub>	53.1	51.8	51.6	51.6	48.4	52.4 (0.1)
NO <sub>2</sub> <sup>+</sup>	230.6	227.7	227.6	227.6	221.7	224.8 (0.2)
N <sub>3</sub>	61.4	61.2	61.1	61.0	55.3	61.8 (0.2)
O <sub>2</sub>	13.2	13.0	12.6	DNF	9.0	10.4 (0.2)
O <sub>3</sub>	62.0	61.8	61.2	DNF	50.0	48.5 (0.1)
ClO	54.0	52.4	52.0	51.9	48.5	52.5 (0.1)
ClO <sub>2</sub>	58.0	52.6	50.8	49.9	49.7	54.7 (0.2)
SO <sub>2</sub>	41.1	35.3	33.5	32.7	27.2	25.5 (0.2)
Cl <sub>2</sub>	70.6	66.1	65.2	65.0	54.3	55 (2)
Ave dev	7.2	5.4	5.2	4.7	2.5	—

DNF, the data did not fit the extrapolation function; Ave dev, the average absolute deviation from the experiment.

<sup>a</sup> Reference 62.

<sup>b</sup> References 65, 70–77, and 91–96.

<sup>c</sup> Ionization potential of NO.

**TABLE VI.**  
**Comparison of Calculated and Experimental Atomization Energies (kcal / mol) for Series of Small Inorganic Molecules.**

	Basis Set			Expt <sup>a</sup>
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	
NO	149.2	151.7	152.7	150.1
NO <sub>2</sub>	223.2	226.2	227.8	—
N <sub>3</sub>	234.5	302.5	304.1	—
O <sub>2</sub>	120.3	120.8	121.7	118.0
O <sub>3</sub>	134.4	135.4	136.7	142.2 ± 0.5
ClO	59.2	63.0	64.2	63.3
ClO <sub>2</sub>	100.8	115.8	116.1	121.0 ± 1.5
SO <sub>2</sub>	215.6	235.9	242.3	254.0
Cl <sub>2</sub>	50.0	53.2	54.1	57.2
Ave				
dev	11.6	5.5	4.6	—

Ave dev, the average absolute deviation from the experiment.

<sup>a</sup> References 63, 98, and 99.

experiment with an average absolute deviation from experiment of 36 cm<sup>-1</sup>. Scott and Radom found that scaling the vibrational frequencies obtained by the B3LYP method and 6-31G(*d*) basis set by 0.9614 yields better agreement with the experiment.<sup>97</sup> However, while it is common practice to scale calculated vibrational frequencies, it should be mentioned that scaling factors are both method and basis set dependent. Because no appropriate scaling factor for this particular combination has been reported to our knowledge, frequencies reported in this study will remain unscaled.

## Conclusions

A study of numerous small inorganic molecules using the hybrid HF/DF B3LYP method and Dunning et al.'s correlation-consistent aug-cc-pVXZ (*X* = *D*, *T*, *Q*, 5) basis sets was done to test the method and basis set compatibility and to test the convergence of calculated values with increasing basis set size. Bond distances, bond angles, dipole moments, electron affinities, and harmonic vibrational frequencies were calculated using various size basis sets; and nonlinear regression was used to extrapolate the results to the CBS limit. The results showed that the union of the HF/DF B3LYP method and Dunning et al.'s correlation-consistent basis sets does indeed yield results that are not

only comparable to the experiment, but are also often comparable to other computational studies found in the literature. Furthermore, it was shown that as the basis set size increases from the double-zeta level there are marked changes in structural parameters and electron affinities. However, increasing the basis set beyond the quadruple-zeta level up to the quintuple-zeta elicited negligible changes in bond lengths and electron affinities. One should also note that there was no marked change in the extrapolation of these values to the CBS limit by adding the fourth data point attained from the quintuple-zeta basis set and this further increase in basis set size was not worth the subsequent demand on computational resources. Finally, it can be seen that when coupled with the B3LYP method, the aug-cc-pVTZ basis set is generally sufficient for the direct calculation of many molecular properties for the molecules studied. However, if one wishes to extrapolate the values to the CBS limit, the function used requires calculation at the aug-cc-pVQZ level. Further exploration using other extrapolation techniques and other functionals should also prove worthwhile.

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**TABLE VII.** Comparison of Calculated and Experimental Normal Modes of Vibration (cm<sup>-1</sup>) for Series of Small Inorganic Molecules.

	Basis Set				Expt <sup>a</sup>
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	
NO	1975	1968	1974	1974	1875
NO <sup>+</sup>	2473	2477	2481	2482	2377
NO <sub>2</sub> <sup>-</sup>	790	796	799	—	828
	1306	1284	1293	—	1261
	1338	1325	1331	—	1328
NO <sub>2</sub>	754	766	768	—	750
	1394	1386	1392	—	1318
	1705	1688	1694	—	1618
NO <sub>2</sub> <sup>+</sup>	629	564	651	—	570
	629	564	651	—	570
	1445	1447	1450	—	1396
N <sub>3</sub>	472	508	505	—	—
	582	614	613	—	—
	1372	1374	1377	—	—
	1716	1702	1705	—	—
N <sub>3</sub> <sup>-</sup>	628	660	659	—	645
	628	660	659	—	645
	1352	1356	1358	—	1344
	2074	2072	2074	—	2041
O <sub>2</sub>	1645	1626	1636	—	1555
O <sub>2</sub> <sup>-</sup>	1626	1164	1169	—	—
O <sub>3</sub>	748	746	751	—	705
	1213	1191	1205	—	1042
	1263	1250	1259	—	1110
O <sub>3</sub> <sup>-</sup>	596	596	601	—	—
	880	876	884	—	—
	1059	1056	1062	—	—
ClO	842	854	857	—	854
ClO <sup>-</sup>	641	649	650	—	—
ClO <sub>2</sub>	406	438	448	—	445
	883	933	951	—	943
	989	1066	1093	—	1111
ClO <sub>2</sub> <sup>-</sup>	333	355	364	—	400
	737	767	779	—	790
	769	811	827	—	840
SO <sub>2</sub>	485	514	520	—	518
	1102	1159	1169	—	1151
	1258	1341	1359	—	1362
SO <sub>2</sub> <sup>-</sup>	417	444	452	—	—
	925	969	979	—	—
	993	1054	1070	—	—
Cl <sub>2</sub>	529	539	540	—	557
Cl <sub>2</sub> <sup>-</sup>	198	200	202	—	—
Ave					
dev	54	37	36	—	

Ave dev, the average absolute deviation from the experiment.  
<sup>a</sup> References 75 and 100–113.



## References

1. Dunning, T. H. J. *J Chem Phys* 1989, 90, 1007.
2. Pople, J. A.; Frisch, M. J.; Luke, B. T.; Binkley, J. S. *Int J Quantum Chem Quantum Chem Symp* 1983, 17, 307.
3. Sinanoglu, O. In *Advances in Chemistry and Physics*; Prigogine, I., Ed.; Wiley: London, 1964; Vol. 6; p 315.
4. McWeeny, R. *The New World of Quantum Chemistry*; D. Reidel: Dordrecht, 1976.
5. Mok, D. K. W.; Neumann, R.; Handy, N. C. *J Phys Chem* 1996, 100, 6225.
6. Ziegler, T. *Chem Rev.* 1991, 91, 651.
7. Krishna, M. V. R. *J Comput Chem* 1990, 11, 629.
8. Savin, A. *Int J Quantum Chem* 1988, S22.
9. Tschinke, V.; Ziegler, T. *J Chem Phys* 1990, 93, 8051.
10. Erdahl, R.; Smith, V. H., Eds.; *Density Matrices and Density Functionals*; Reidel: Dordrecht, 1987.
11. Becke, A. D. *J Chem Phys* 1993, 98, 5648.
12. Gervy, D.; Verhaegen, G. *Int J Quantum Chem* 1997, 12, 115.
13. Pettersson, L. G. M.; Siegbahn, P. E. M. *J Chem Phys* 1985, 83, 3538.
14. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J Chem Phys* 1980, 72, 650.
15. Jankowski, K.; Becherer, R.; Scharf, P.; Schiffer, H.; Ahlrichs, R. *Chem Phys* 1985, 82, 1413.
16. Ahlrichs, R.; Scharf, P.; Jankowski, K. *Chem Phys Lett* 1985, 98, 381.
17. Becherer, R.; Ahlrichs, R. *Chem Phys* 1985, 99, 389.
18. Almlof, J.; Taylor, P. R. *J Chem Phys* 1987, 86, 4070.
19. Almlof, J.; Helgaker, T.; Taylor, P. R. *J Phys Chem* 1988, 92, 3029.
20. Scheiner, A. C.; Baker, J.; Andzelm, J. W. *J Comput Chem* 1997, 18, 775.
21. Woon, D. E.; Dunning, T. H. Jr. *J Chem Phys* 1993, 98, 1358.
22. Kendall, R. A.; Dunning, T. H. Jr.; Harrison, R. J. *J Chem Phys* 1992, 96, 6796.
23. Feller, D. *J Chem Phys* 1992, 96, 6104.
- 24a. Xantheas, S. S.; Dunning, T. H. Jr. *J Phys Chem* 1993, 97, 18.
- 24b. Xantheas, S. S.; Dunning, T. H. Jr. *J Phys Chem* 1993, 97, 6616.
- 25a. Wilson, A. K.; Dunning, T. H. Jr. *J Chem Phys* 1997, 106, 8718.
- 25b. Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem Phys Lett* 1998, 286, 243.
- 25c. Martin, J. M. L. *Chem Phys Lett* 1998, 259, 669.
26. Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J Chem Phys* 1985, 82, 890.
27. Chong, D. P.; Langhoff, S. R. *J Chem Phys* 1986, 84, 5606.
28. Frisch, M. J.; Trucks, H. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomeperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision B.3)*; Gaussian, Inc.: Pittsburgh, PA, 1994.
29. Kohn, W.; Becke, A. D.; Parr, R. G. *J Phys Chem* 1996, 100, 12974.
30. Becke, A. D. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Vol. 2, p 1022.
31. Ernzerhof, M.; Perdew, J. P.; Burke, K. *Topics Curr Chem* 1996, 180, 1.
32. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J Phys Chem* 1994, 98, 11623.
33. Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.
34. Becke, A. *Phys Rev A* 1988, 38, 3098.
35. Vosko, S. H.; Wilk, L.; Nusair, M. *Can J Phys* 1980, 58, 1200.
36. Becke, A. D. *J Chem Phys* 1993, 98, 1372.
37. Perdew, J. P. *Phys Rev B* 1986, 33, 8822.
38. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
39. Bauschlicher, C. W.; Partridge, H. *J Chem Phys* 1995, 103, 1788.
40. Bauschlicher, C. W. Jr. *Chem Phys Lett* 1995, 246, 40.
41. Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2 ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.
42. Rauhut, G.; Pulay, P. *J Phys Chem* 1995, 99, 3093.
43. Ruiz, E.; Salahub, D. R.; Vela, A. *J Phys Chem* 1996, 100, 12265.
44. Qin, Y.; Wheeler, R. A. *J Chem Phys* 1994, 102, 1689.
45. Qin, Y.; Wheeler, R. A. *J Phys Chem* 1996, 100, 10554.
46. Walden, S. E.; Wheeler, R. A. *J Chem Soc Perkin Trans* 1996, 2, 2663.
47. Walden, S. E.; Wheeler, R. A. *J Phys Chem* 1996, 100, 1530.
48. Walden, S. E.; Wheeler, R. A. *J Am Chem Soc* 1997, 119, 3175.
49. Wise, K. E.; Grafton, A. K.; Wheeler, R. A. *J Phys Chem A* 1997, 101, 1160.
50. Walden, S. E.; Wheeler, R. A. *J Chem Soc Perkin Trans* 1996, 2, 2653.
51. Grafton, A. K.; Boesch, S. E.; Wheeler, R. A. *J Mol Struct (Theochem)* 1997, 392, 1.
52. Grafton, A. K.; Wheeler, R. A. *J Phys Chem A* 1997, 101, 7154.
53. Boesch, S. E.; Wheeler, R. A. *J Phys Chem* 1995, 99, 8125.
54. Boesch, S. E.; M.S. Thesis, University of Oklahoma, Norman, OK, 1996.
55. Boesch, S. E.; Wheeler, R. A. *J Phys Chem A* 1997, 101, 5799.
56. Boesch, S. E.; Wheeler, R. A. *J Phys Chem A* 1997, 101, 8351.
57. Boesch, S. E.; Grafton, A. K.; Wheeler, R. A. *J Phys Chem* 1996, 100, 10083.
58. Engels, B.; Eriksson, L. A.; Lunell, S. *Adv Quantum Chem* 1996, 27, 297.

59. Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. In *Modern Density Functional Theory: A Tool for Chemistry*; Seminario, J. M.; Politzer, P. Eds.; Elsevier Science B.V.: Dordrecht, 1995; Vol. 2, p 273.
60. Barone, V. *Theor Chim Acta* 1995, 91, 113.
61. Sherrod, P. H. *NLREG, Non-Linear Regression Analysis Program*. S & H Computer Systems: Nashville, 1995.
62. Ebersson, L.; Gonzalez-Luque, R.; Lorentzon, J.; Merchan, M.; Roos, B. O. *Chem Soc* 1993, 115, 2898.
63. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J Chem Phys* 1991, 94, 7221.
64. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*, Vol. 4. Constants of Diatomic Molecules; Van Nostrand: Princeton, NJ, 1979.
65. Edqvist, O.; Asbrink, L.; Lindholm, E. *Z Naturforsch A* 1971, 26, 1407.
66. Keck, D. B.; Hause, C. D. *J Mol Spectrosc* 1968, 26, 163.
67. Lippard, S. J., Ed. *Progress in Inorganic Chemistry*; Wiley: New York, 1980; Vol. 27, p 465.
68. Truter, M. R.; Cruickshank, D. W.; Jeffrey, G. *Acta Crystallogr* 1960, 13, 855.
69. Morino, Y.; Tanimoto, M.; Saito, S.; Hirota, E.; Awata, R.; Tanaka, T. *J Mol Spectrosc* 1983, 98, 331.
70. Douglas, A. E. *Can J Phys* 1965, 43, 2216.
71. Polak, M. K.; Gruebele, M.; Sayakally, R. J. *J Am Chem Soc* 1984, 109, 2884.
72. Continetti, R. E.; Cyr, D. R.; Metz, R. B.; Neumark, D. M. *Chem Phys Lett* 1991, 182, 406.
73. Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem Phys Lett* 1989, 164, 449.
74. Wang, L. W.; Woo, S. B.; Helmy, E. M. *Phys Rev A* 1987, 35, 759.
75. Herzberg, G. *Molecular Spectra and Molecular Structure*. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules; Van Nostrand: New York, 1966; Vol. 3.
76. Morino, Y.; Kikuchi, Y.; Saito, S.; Hirota, E. *J Mol Spectrosc* 1964, 13, 95.
77. Nimlos, M. R.; Ellison, G. B. *J Phys Chem* 1986, 90, 2574.
78. Jones, H.; Brown, J. M. *J Mol Spectrosc* 1972, 17, 222.
79. Arnau, J. L.; Giguere, P. A.; Morissette, S. *Can J Spectrosc* 1972, 17, 63.
80. Kiyazaki, K.; Tanoura, M.; Tanaka, K.; Tanaka, T. *J Mol Spectrosc* 1986, 115, 435.
81. Altshuller, A. P. *J Chem Phys* 1956, 24, 642.
82. Chen, E. C.; Wentworth, W. E. *J Phys Chem* 1985, 89, 4099.
83. Dunitz, J. D.; Hedberg, K. *J Am Chem Soc* 1950, 72, 3108.
84. Edwards, H. G. M.; Good, E. A. M.; Long, D. A. *J Chem Soc Faraday Trans II* 1976, 72, 865.
85. Andrews, L.; Raymond, J. I. *J Chem Phys* 1971, 55, 3087.
86. Amano, T.; Hirota, E.; Morino, Y. *J Mol Spectrosc* 1968, 27, 257.
87. Hellwege, K. H., Ed. *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: New York, 1974; Vol. Group II, Vol. 6, Molecular Constants.
88. Nelson, R. D.; Like, D. R.; Maryott, A. A. *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*; National Standard Reference Data Service; National Bureau of Standards: Washington, DC, 1967; Vol. 10.
89. Hellwege, K. H., Ed. *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: Heidelberg, Germany, 1982; Vol. Group II, Vol. 14, Subvol. a.
90. McClellan, A. L. *Tables of Experimental Dipole Moments*; Freeman: San Francisco, CA, 1963.
91. Erwin, K. M.; Ho, J.; Lineberger, W. C. *J Phys Chem* 1988, 92, 5405-5412.
92. Brundle, C. R.; Neumann, D.; Price, W. C.; Evans, D.; Potts, A. W.; Streets, D. G. *J Chem Phys* 1970, 53, 705.
93. Alekseev, V. I.; Zyubina, T. S.; Zyubin, A. S.; Baluev, A. V. *Izv Akad Nauk SSSR Ser Khim* 1989, 10, 2278.
94. Babcock, L. M.; Pentecost, T.; Koppenol, W. H. *J Phys Chem* 1989, 93, 8126.
95. Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J Chem Phys* 1992, 96, 8012.
96. Chupka, W. A.; Berkowitz, J.; Gutman, D. *J Chem Phys* 1971, 55, 2724.
97. Scott, A. P.; Radom, L. *J Phys Chem* 1996, 100, 16502.
- 98a. Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J Chem Phys* 1989, 90, 5622.
- 98b. Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J Chem Phys* 1990, 93, 2537.
99. For example (a) Martin, J. M. L. *J Chem Phys* 1998, 108, 2791. (b) Bauschlicher, C. W.; Ricca, A. *J Phys Chem A* 1998, 102, 8044.
100. Richter-Addo, G.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.
101. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1963.
102. Gray, P.; Waddington, T. C. *Trans Faraday Soc* 1957, 53, 901.
103. Papazian, H. A. *J Chem Phys* 1961, 34, 1614.
104. Soulen, J. R.; Schwartz, W. F. *J Phys Chem* 1962, 66, 2066.
105. Nebgen, J. W.; McElroy, A. D.; Klodowski, H. F. *Inorg Chem* 1965, 4, 1796.
106. Wilson, M. K.; Badger, R. M. *J Chem Phys* 1948, 16, 741.
107. Herman, K.; Giguere, P. A. *Can J Chem* 1965, 43, 1746.
108. Nielsen, A. H.; Woltz, P. J. H. *J Chem Phys* 1952, 20, 1878.
109. Mathieu, J. P. *Compt Rend* 1952, 234, 2272.
110. Arakawa, E. T.; Nielsen, A. H. *J Mol Spectrosc* 1958, 2, 413.
111. Weston, R. E.; Broadasky, T. F. *J Chem Phys* 1957, 27, 683.
112. Shelton, R. D.; Nielsen, A. H.; Fletcher, W. H. *J Chem Phys* 1953, 21, 2178.
113. Grigg, E. C. M.; Johnston, G. R. *Aust J Chem* 1966, 19, 1147.